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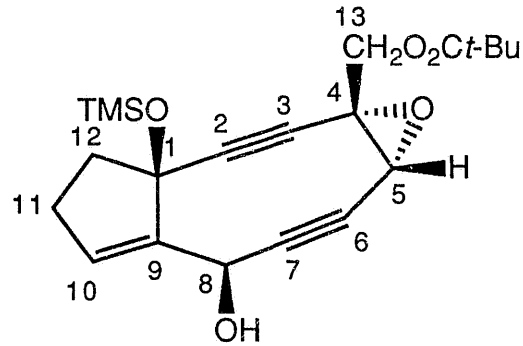
Supporting Information for *J. Am. Chem. Soc.*, **1992**, 114(3), 1086-1087, DOI: 10.1021/ja00029a046

MYERS
1086-1087

J-1087-m1

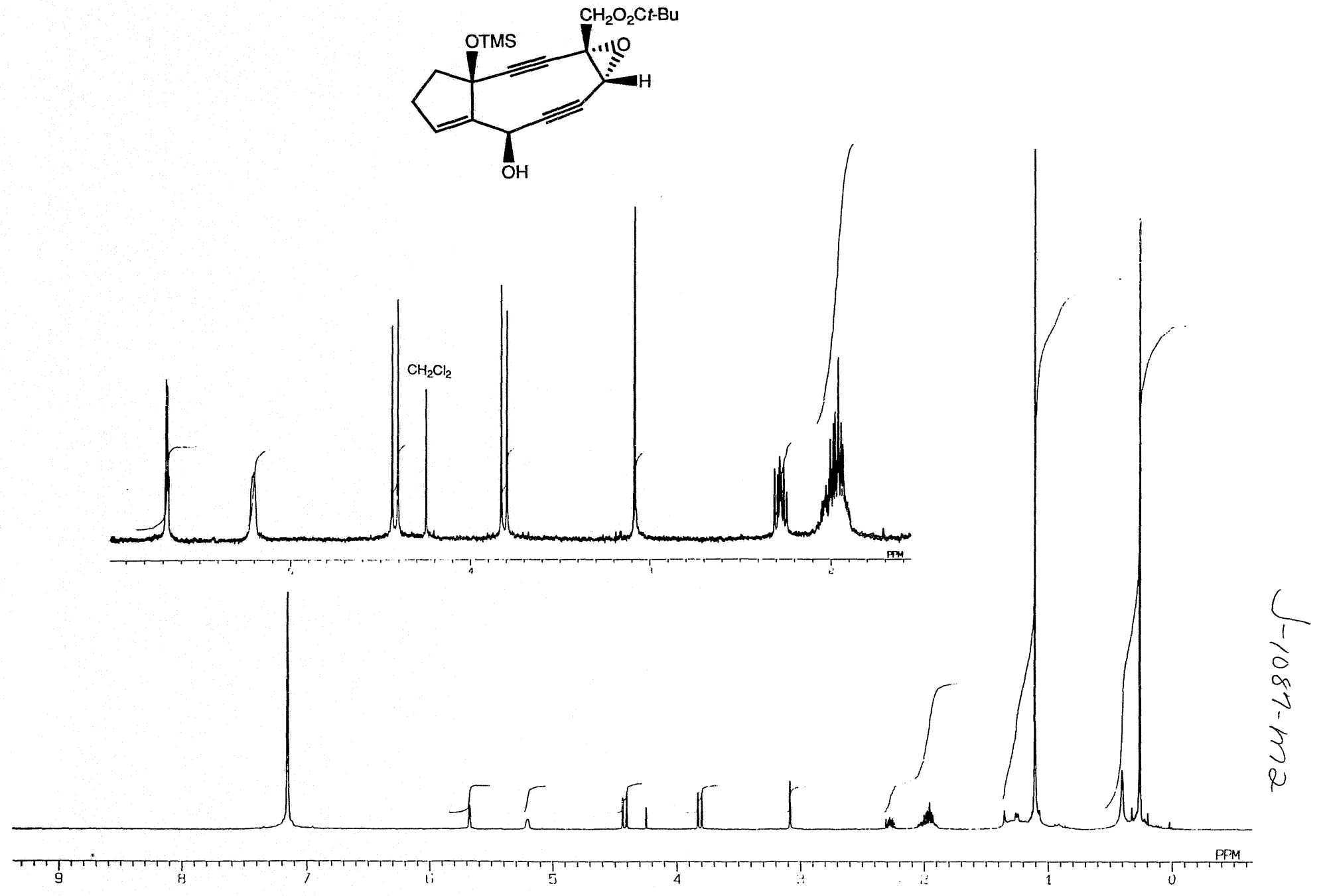


^{1}H NMR (400 MHz, C_6D_6): 5.68 (dd, 1H, *J*~1.5, 2.0 Hz, H10)
5.20 (bs, 1H, H8)
4.42 (d, 1H, *J*=12.4 Hz, H13)
3.81 (d, 1H, *J*=12.4 Hz, H13)
3.09 (s, 1H, H5)
2.24-2.31 (m, 1H, H11)
1.93-2.03 (m, 3H, H11, H12)
1.11 (s, 9H, O_2C*t*-Bu)
0.26 (s, 9H, $Si(CH_3)_3$)

FTIR (neat film, cm^{-1}): 3444(b), 2210(w), 1738(s), 1252(m), 1142(s).

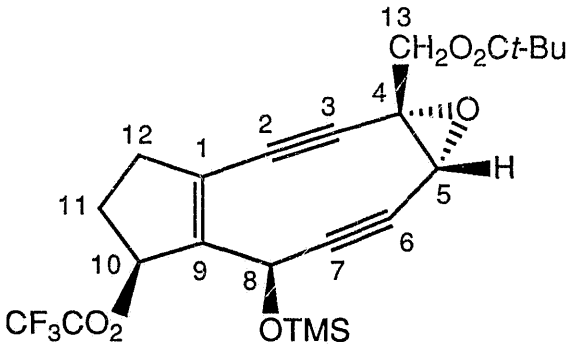
TLC (1:1 Et_2O:pet ether): R_f = 0.32

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 389.1784 $[MH]^+$
found: 389.1795



J-10877-172

J-1087-m23

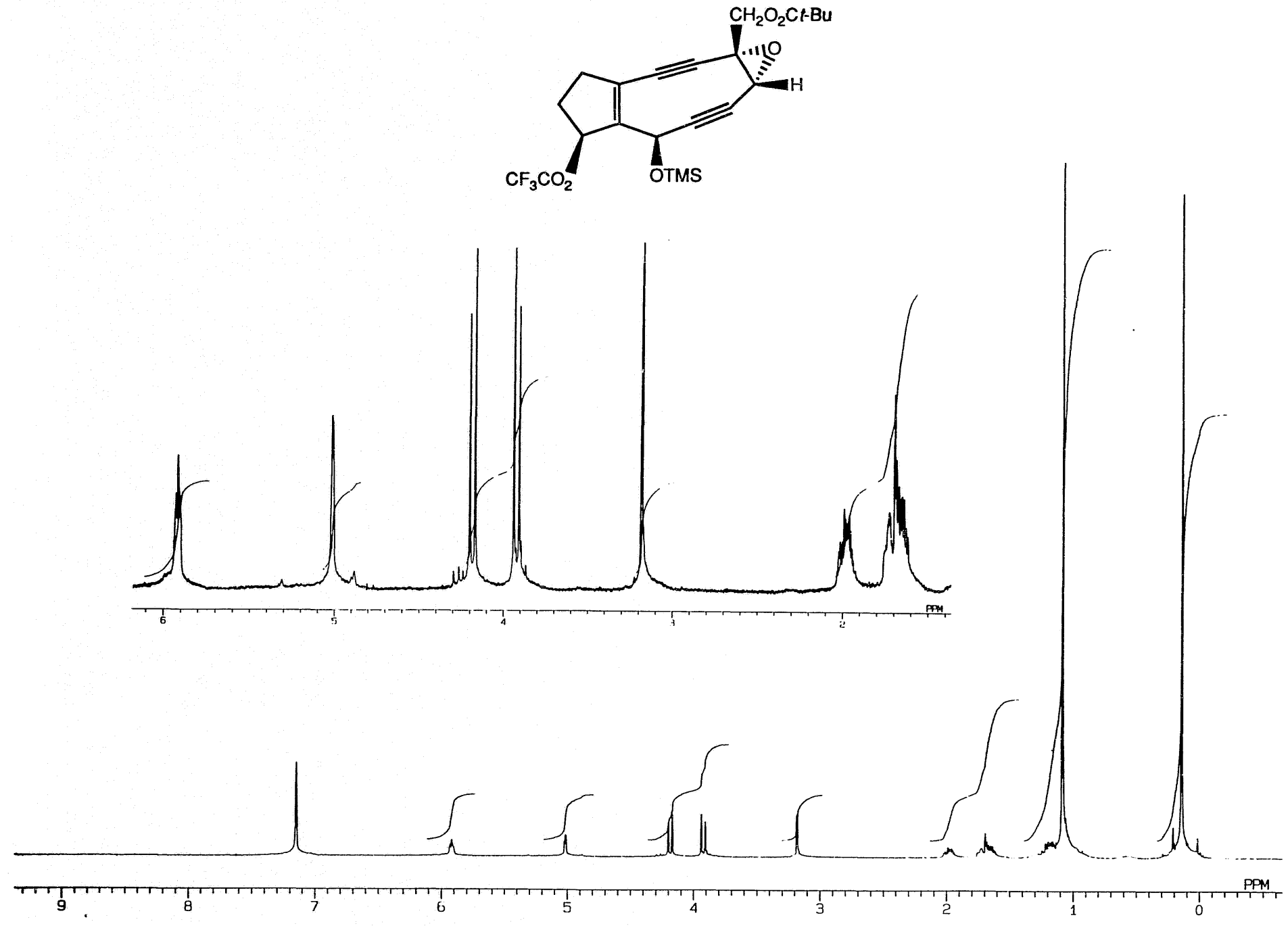


^{1}H NMR (400 MHz, C_6D_6): 5.92 (bd, 1H, J=4.4 Hz, H10)
5.02 (bs, 1H, H8)
4.19 (d, 1H, J=12.2 Hz, H13)
3.93 (d, 1H, J=12.2 Hz, H13)
3.18 (d, 1H, J=1.5 Hz, H5)
1.95-2.03 (m, 1H, H11)
1.62-1.75 (m, 2H, H12)
1.15-1.24 (m, 1H, H11)
1.09 (s, 9H, O_2Ct-Bu)
0.15 (s, 9H, $Si(CH_3)_3$)

FTIR (neat film, cm^{-1}): 1784(s), 1741(m), 1146(s)

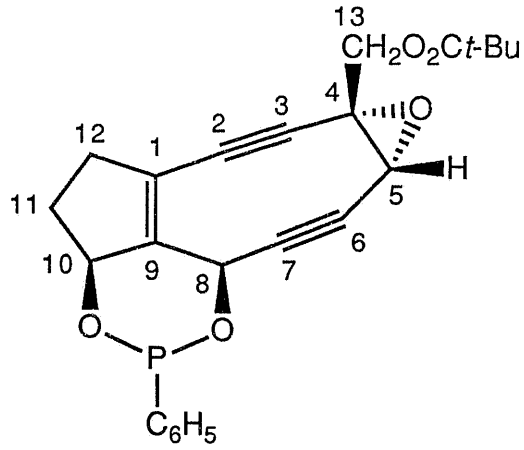
TLC (20% EtOAc-Hexanes): R_f = 0.53

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 485.1607 $[MH]^+$
found: 485.1617

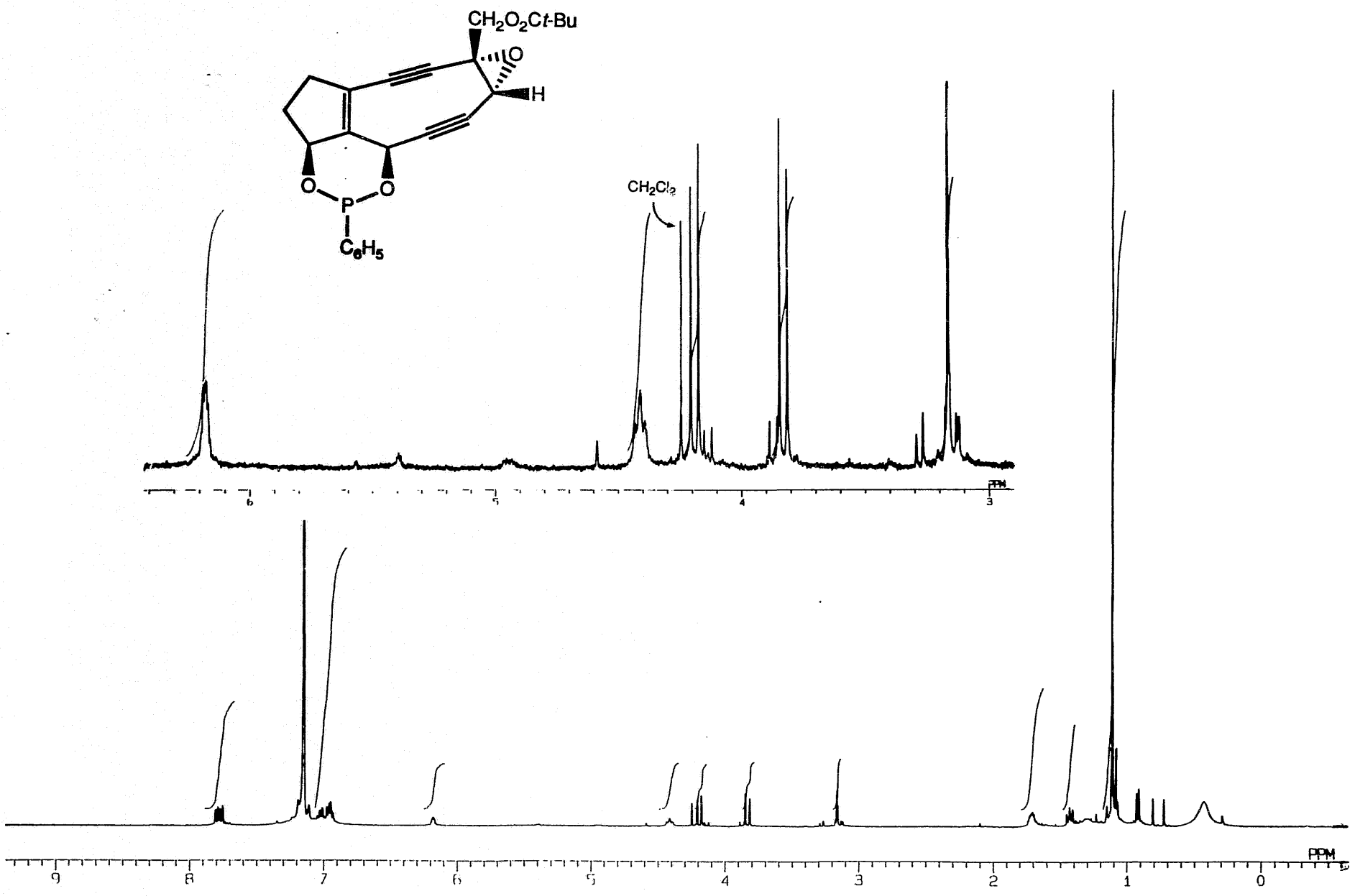


J-10879-HNY

J-1087-m5

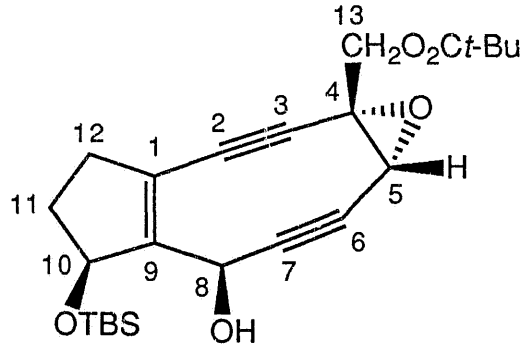


^{1}H NMR (400 MHz, C_6D_6):	7.78 (ddd, 2H, *J*=1.5, 8.3, 9.8 Hz, *o*-Ar)
	6.91-7.06 (m, 3H, Ar)
	6.16-6.20 (m, 1H, H8)
	4.37-4.45 (m, 1H, H10)
	4.19 (d, 1H, *J*=12.4 Hz, H13)
	3.83 (d, 1H, *J*=12.4 Hz, H13)
	3.16 (d, 1H, *J*=0.7 Hz, H5)
	1.68-1.74 (m, 2H, H11 or H12)
	1.39-1.46 (m, 2H, H11 or H12)
	1.11 (s, 9H, O_2C*t*-Bu)
FTIR (neat film, cm^{-1}):	2190(w), 1733(s), 1354(m), 1277(s), 1132(s)
TLC (1:2 EtOAc:Hexanes):	R_f = 0.23
HR FAB MS	
(matrix: Nitrobenzyl alcohol):	calcd: 439.1311 $[M + O + H]^+$
	found: 439.1335



J-10874-76

J-1087-m7

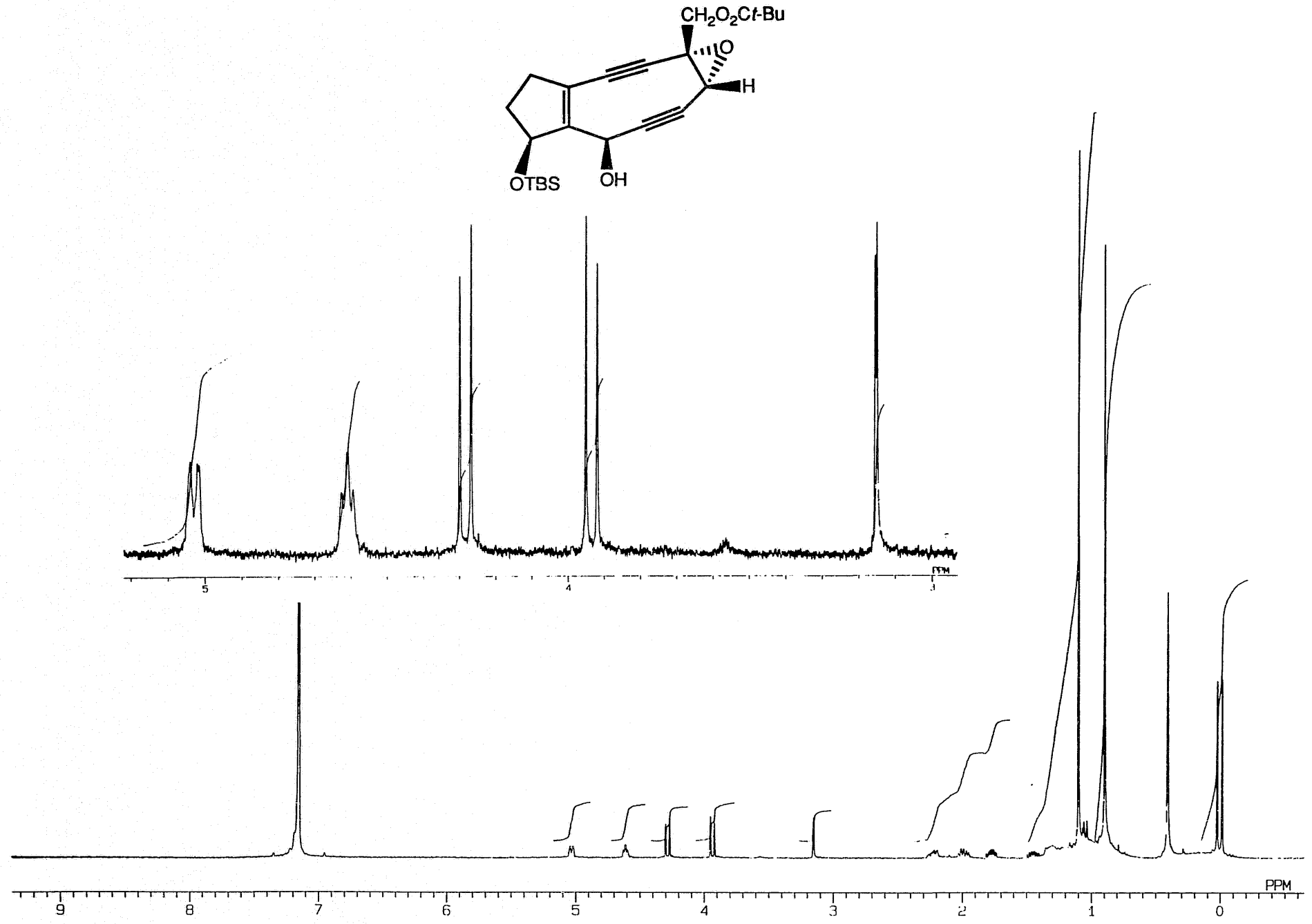


^{1}H NMR (400 MHz, C_6D_6): 5.03 (bdd, 1H, *J*=1.7, 7.6 Hz, H8)
4.58-4.64 (m, 1H, H10)
4.28 (d, 1H, *J*=12.4 Hz, H13)
3.94 (d, 1H, *J*=12.4 Hz, H13)
3.15 (d, 1H, *J*=1.7 Hz, H5)
2.18-2.27 (m, 1H, H12)
1.95-2.03 (m, 1H, H12)
1.73-1.82 (m, 1H, H11)
1.40-1.50 (m, 1H, H11)
1.10 (s, 9H, O_2Ct-Bu)
1.04 (d, 1H, *J*=9.3 Hz, OH)
0.90 (s, 9H, $Si(CH_3)_3$)
0.03 (s, 3H, $SiCH_3$)
- 0.01 (s, 3H, $SiCH_3$)

FTIR (neat film, cm^{-1}): 3422(b), 2188(w), 1738(s), 1149(s)

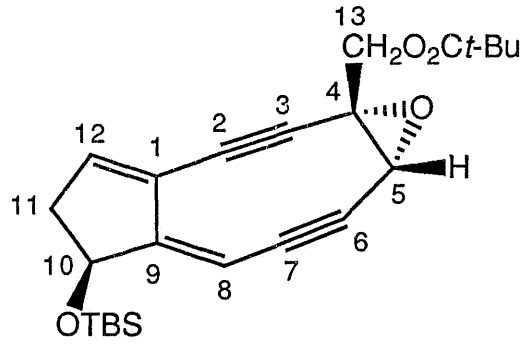
TLC (20% EtOAc-Hexanes): R_f = 0.37

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 431.2254 $[MH]^+$
found: 431.2240



J-10879-mg

J-1087-m9

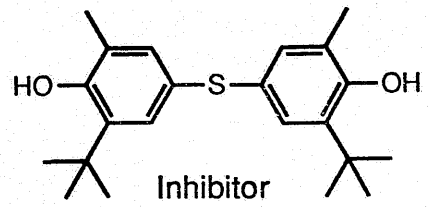


^{1}H NMR (400 MHz, C_6D_6): 5.78 (bs, 1H, H12)
5.49 (bs, 1H, H8)
4.37 (d, 1H, *J*=12.2 Hz, H13)
4.25 (m, 1H, H10)
3.96 (d, 1H, *J*=12.2 Hz, H13)
3.46 (s, 1H, H5)
1.93-2.06 (m, 2H, H11)
1.12 (s, 9H, O_2Ct-Bu)
0.85 (s, 9H, $Si(CH_3)_3$)
- 0.11 (s, 3H, $SiCH_3$)
- 0.13 (s, 3H, $SiCH_3$)

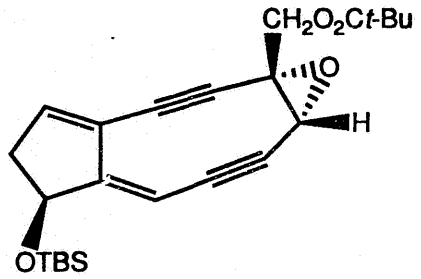
FTIR (neat film, cm^{-1}): 2177(w), 1733(s)

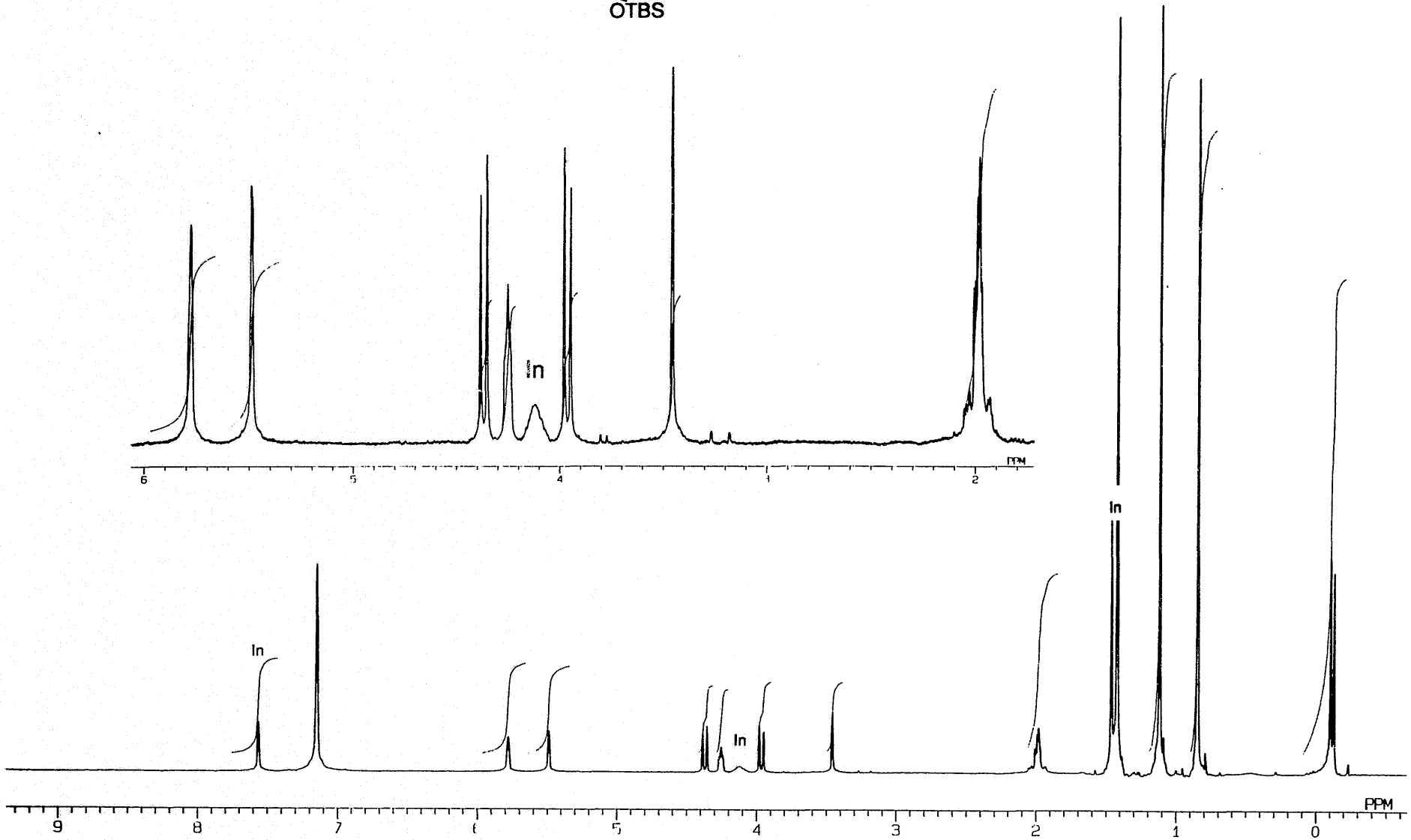
TLC (20% EtOAc-Hexanes): R_f = 0.46

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 413.2148 $[MH]^+$
found: 413.2147



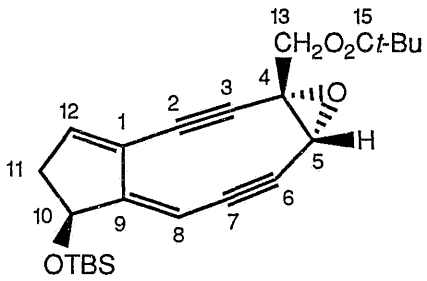
Inhibitor

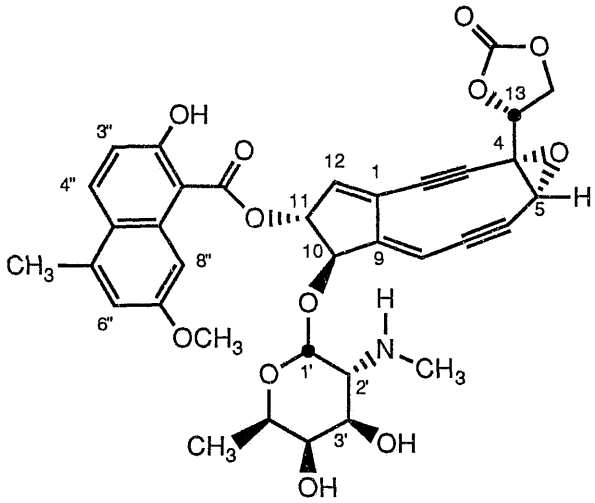




J-1087-hm10

J-1087-m11

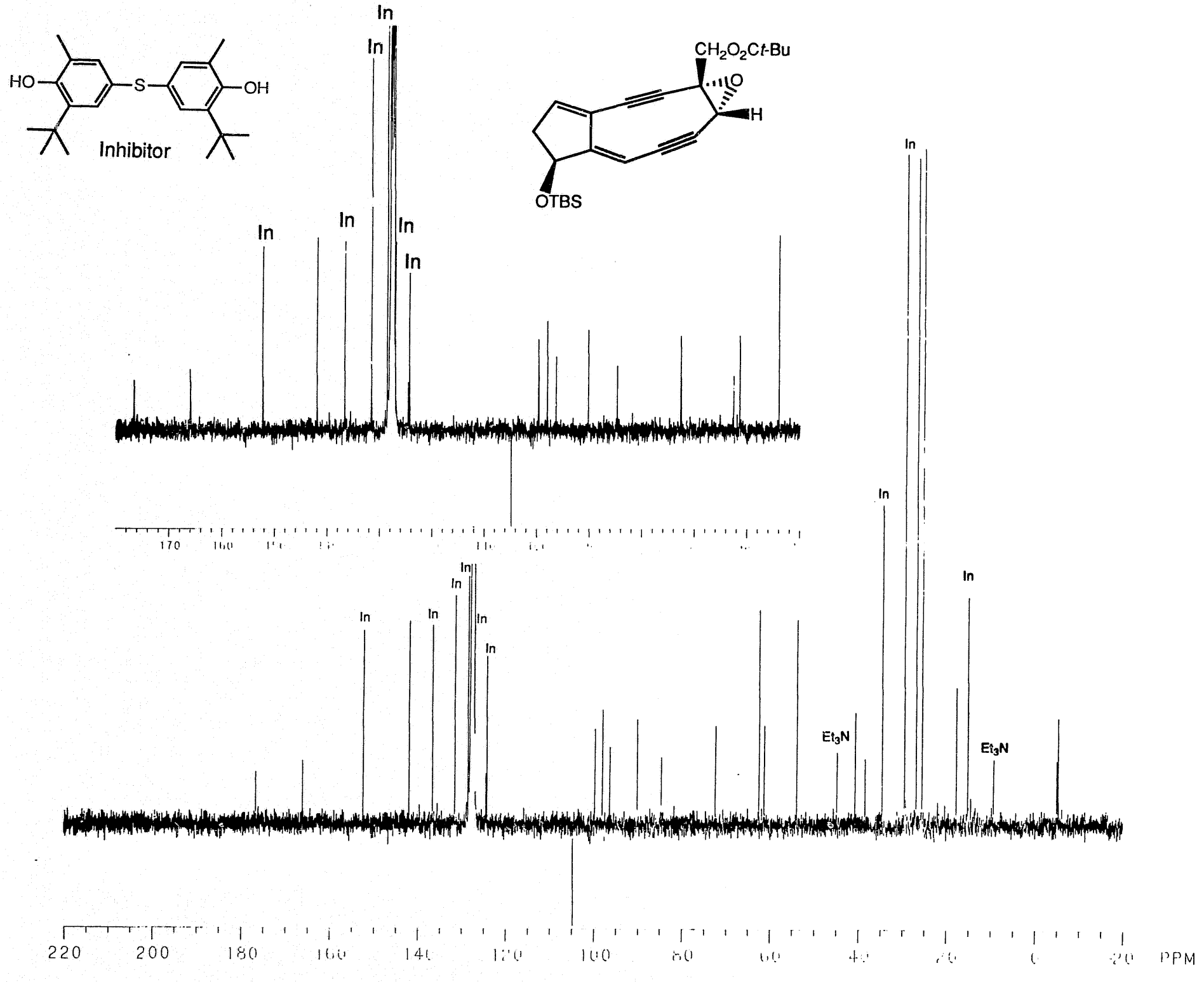




Synthetic (**7**) ^{13}C NMR (300 MHz, C_6D_6)	NCS Chromophore (**1**) ^{13}C NMR (400 MHz, 1:1 CD_3CO_2D:CD_3OD)‡
176.6 (C15)	-
166.0 (C9)	160.2 (C9)
141.9 (C12)	139.4 (C12)
124.5 (C1)	129.8 (C1)
99.8 (C8)†	106.5 (C8)
98.0 (C6)†	99.7 (C6)
96.4 (C3)†	97.6 (C3)
90.2 (C7)†	90.7 (C7)
84.7 (C2)†	87.5 (C2)
72.6 (C10)	82.2 (C10)
62.5 (C13)†	76.1 (C13)
61.3 (C4)†	63.8 (C4)
53.9 (C5)	55.2 (C5)
40.7 (CO-C-$(CH_3)_3$)†	-
38.5 (C11)†	81.6 (C11)
26.8 (CO-C-$(CH_3)_3$)†	-
25.5 (Si-C-$(CH_3)_3$)†	-
17.7 (Si-C-$(CH_3)_3$)	-
- 5.0 ($SiCH_3$)	-
- 5.3 ($SiCH_3$)	-

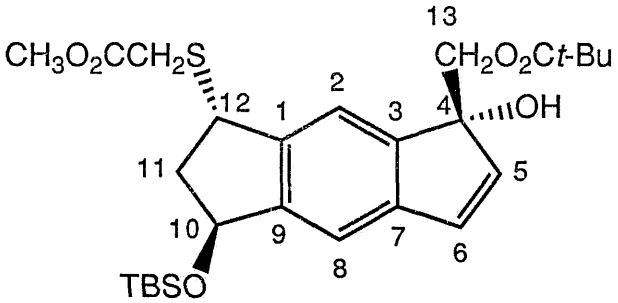
†tentative assignments

‡Edo, K.; Mizugaki, M.; Koide, Y.; Seto, H.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331.


HO
S
OH
Inhibitor
CH2O2Ct-Bu
O
H
OTBS
In
Et3N
220
200
180
160
140
120
100
80
60
40
20
0
-20
PPM

J-10877-m18

J-1087-m13

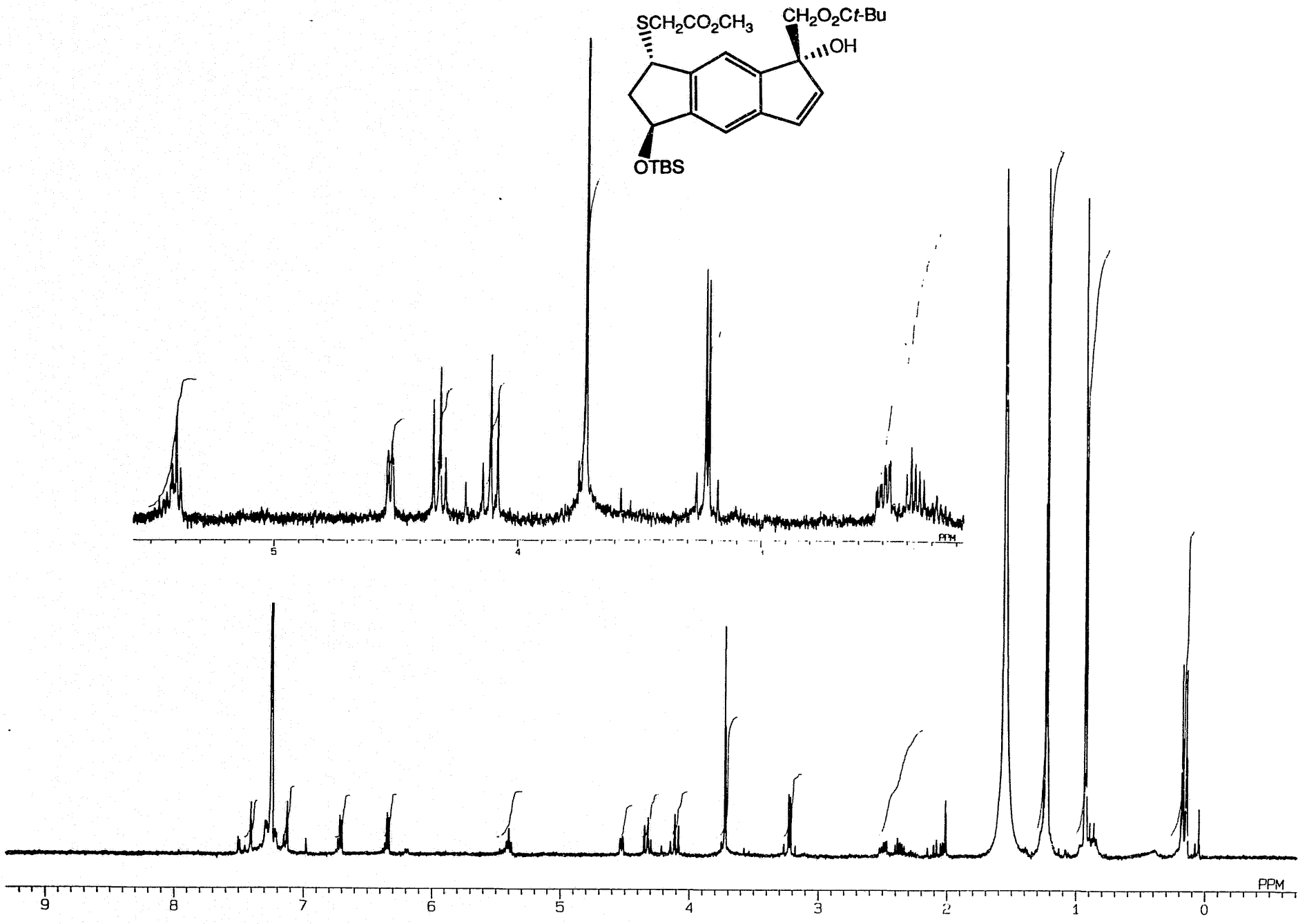


^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (s, 1H, H2)
7.12 (s, 1H, H8)
6.71 (d, 1H, J=5.9 Hz, H6)
6.34 (d, 1H, J=5.9 Hz, H5)
5.40 (t, 1H, J=6.8±0.3 Hz, H10)
4.52 (dd, 1H, J=1.7, 6.1 Hz, H12)
4.33 (d, 1H, J=11.4 Hz, H13)
4.10 (d, 1H, J=11.4 Hz, H13)
3.72 (s, 3H, CO_2CH_3)
3.22 (AB, 2H, J=14.9 Hz, SCH_2)
2.50 (ddd, 1H, J=1.7, 6.4, 8.4 Hz, H11)
2.32-2.42 (m, 1H, H11)
1.22 (s, 9H, O_2Ct-Bu)
0.92 (s, 9H, $Si(CH_3)_3$)
0.17 (s, 3H, $SiCH_3$)
0.14 (s, 3H, $SiCH_3$)

FTIR (neat film, cm^{-1}): 3452(b), 1734(s), 1717(s), 1532(m), 1349(m)

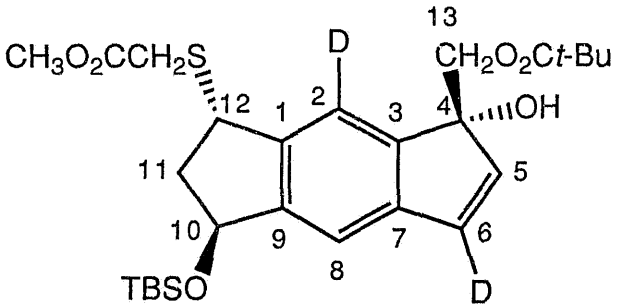
TLC (1:2 EtOAc:Hexanes): R_f = 0.37

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 519.2237 $[M - H]^+$
found: 519.2271



J-1087-MM4

J-1087-m15

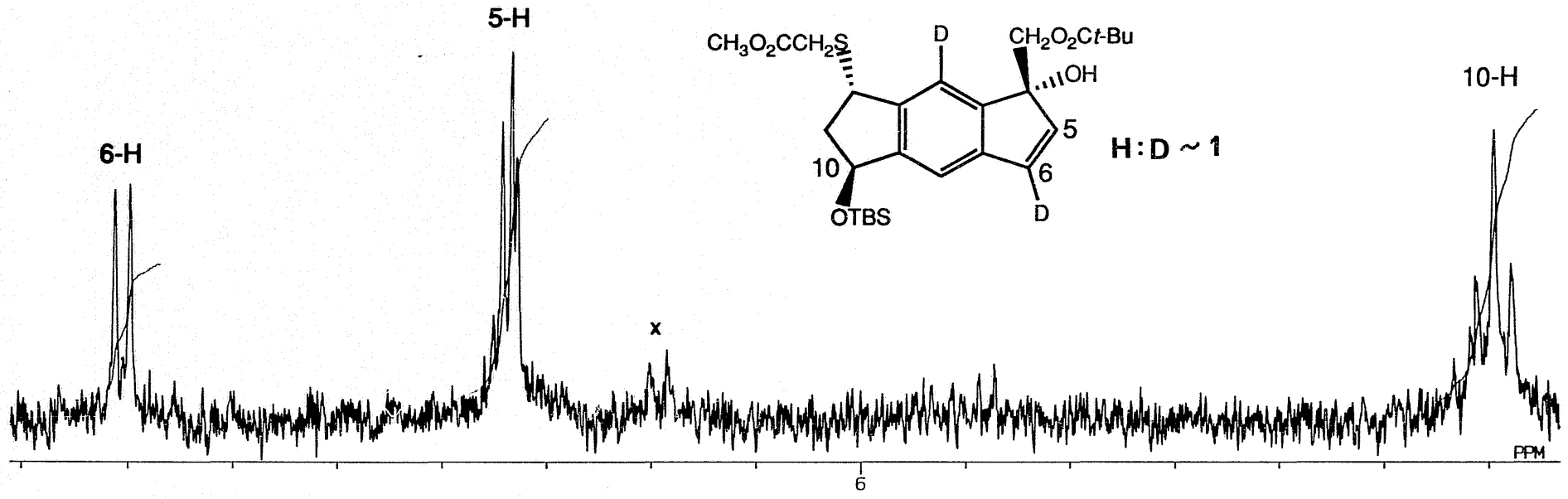


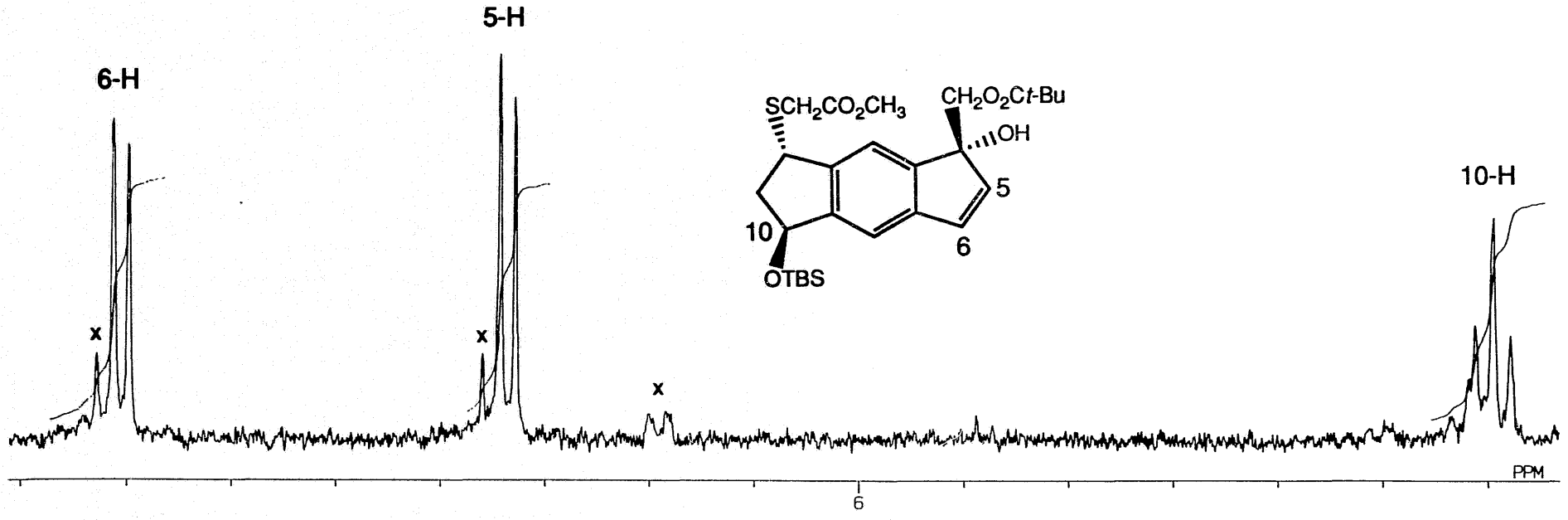
^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (s, 0.5H, H2)
7.12 (s, 1H, H8)
6.71 (d, 0.5H, *J*=5.6 Hz, H6)
6.35 (d, 0.5H, *J*=5.6 Hz, H5)
6.33 [s, 0.5 H, H5(D6)]
5.40 (t, 1H, *J*=6.8±0.3 Hz, H10)
4.52 (dd, 1H, *J*=2.2, 7.6 Hz, H12)
4.33 (d, 1H, *J*=11.2 Hz, H13)
4.10 (d, 1H, *J*=11.2 Hz, H13)
3.72 (s, 3H, CO_2CH_3)
3.22 (AB, 2H, *J*=14.4 Hz, SCH_2)
2.50 (ddd, 1H, *J*=2.2, 6.5, 8.6 Hz, H11)
2.32-2.42 (m, 1H, H11)
1.22 (s, 9H, O_2Ct-Bu)
0.92 (s, 9H, $Si(CH_3)_3$)
0.17 (s, 3H, $SiCH_3$)
0.14 (s, 3H, $SiCH_3$)

FTIR (neat film, cm^{-1}): 3485(b), 1732(m), 1716(s), 1532(m)

TLC (1:2 EtOAc:Hexanes): R_f = 0.37

HR FAB MS
(matrix: Nitrobenzyl alcohol): calcd: 523.2519 $[MH]^+$
found: 523.2560





J-10879-m16

J-1087-M17

Proton NMR spectra recorded on a JEOL JNM-GX400 instrument
Solvent: Acetic acid-d_4. Reference: Acetic acid at 2.04 ppm. Digital resolution: 0.24 Hz

Proton NMR data NCS Chromophore(**1**)					Proton NMR data of Nitrosoamine(**2**)				
	δ	m	# of H	*J* (Hz)		δ	m	# of H	*J* (Hz)
4"	8.09	d	1H	9.2	4"	8.06	d	1H	8.8
8"	7.89	d	1H	2.2	8"	7.86	d	1H	2.2
3"	7.03	d	1H	9.2	3"	7.02	d	1H	8.8
6"	6.90	d	1H	1.2	6"	6.87	d	1H	1.5
12	6.79	s	1H		12	6.73	s	1H	
11	6.36	s	1H		11	5.92	s	1H	
						[5.96	s	1H]†	
8	5.78	s	1H		8	5.72	s	1H	
						[5.71	s	1H]†	
1'	5.77	s	1H		1'	5.58	d	1H	3.6
						[5.36	d	1H	3.7]†
10	5.08	s	1H		10	4.98	s	1H	
13	4.90	dd	1H	5.5, 8.5	13	4.89	dd	1H	5.5, 8.5
14a	4.72	t	1H	8.5	14a	4.71	t	1H	8.5
14b	4.53	dd	1H	5.5, 8.5	14b	4.54	dd	1H	5.5, 8.5
3'	4.40	dd	1H	3.2, 10.5	3'	4.60	dd	1H	3.8, 11.3
						[4.49	dd	1H	3.8, 11.3]†
5'	4.11	q	1H	6.6	5'	4.25	q	1H	6.6
						[4.19	q	1H	6.6]†
5	4.08	s	1H		5	4.08	s	1H	
4'	3.93	s	1H		4'	4.06	s	1H	
OCH3	3.83	s	3H		OCH3	3.81	s	3H	
2'	3.78	dd	1H	3.2, 10.6	2'	5.11	dd	1H	3.7, 11.3
						[5.23	dd	1H	3.7, 11.3]†
NCH3	3.03	s	3H		NCH3	3.24	s	3H	
						[3.96	s	3H]†	
5'-CH3	1.27	d	3H	6.6	5'CH3	1.33	d	3H	6.6

†Minor Rotamer (presumed *syn*)

J-1087-M18

^{1}H NMR spectra (400 MHz, CD_3CO_2D) of neocarzinostatin chromophore (**1**, bottom) and neocarzinostatin chromophore nitrosamine (**9**, top). Smaller numerals refer to the *Z*-rotamer, *m* to methylene chloride.